

Diel Flux of Dissolved Carbohydrate in a
Salt Marsh and a Simulated Estuarine Ecosystem

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Diel Flux of Dissolved Carbohydrate in a Salt Marsh and a Simulated Estuarine Ecosystem

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Abstract

The concentrations of total dissolved carbohydrate (TCHO), monosaccharide (MCHO) and polysaccharide (PCHO) were followed over a total of ten diel cycles in a salt marsh and a 13 m³ seawater tank simulating an estuarine ecosystem. Their patterns are compared to those for total dissolved organic carbon (DOC), ΣCO₂, pH, O₂, chlorophyll *a*, phaeopigments and solar radiation. During 5 of the 6 marsh studies, PCHO underwent periods of sustained accumulation starting in the late morning or early afternoon and continuing into the early evening. These periods possibly represent release of recently synthesized PCHO from phototrophs. Similar patterns were not found in the tank although direct associations between TCHO and phaeopigment dynamics suggest that zooplankton excretion was an important source of dissolved carbohydrate. The numbers of planktonic bacteria determined in one tank study increased rapidly during a late morning PCHO pulse and varied inversely with PCHO throughout the afternoon and evening, indicating that they were able to respond rapidly and control natural substrate concentrations on a time scale of a few hours. MCHO fluctuated to a much lesser extent than PCHO at both locations, with levels possibly maintained near the bacterial uptake threshold or in a closely regulated steady state. TCHO concentration changes over 2- to 3-h sampling intervals suggest very rapid net system release and uptake with summer rates frequently exceeding 30 μg C l⁻¹ h⁻¹ in the marsh and 20 μg C l⁻¹ h⁻¹ in the tank.

Introduction

There is a growing realization of the importance of free-living bacteria in marine ecology (Sorokin, 1971a, b; Hoppe, 1976; Sieburth, 1976, 1979; Sieburth *et al.*,

1977; Larsson and Hagström, 1979). The vast majority of these bacteria are not epibacteria associated with particles but are free planktonic cells that utilize dissolved organic substrates (Williams, 1970; Azam and Hodson, 1977). Almost everything known about the rates of supply and uptake of these materials comes from studies on the release of ¹⁴C labeled organic substances by phytoplankton and on the uptake of ¹⁴C and ³H labeled substrates by bacteria. Both of these types of studies employ bottle incubations and other sample handling which may introduce systematic errors or artifacts.

Net rates of supply and uptake of dissolved substances by the total ecosystem can be estimated through direct analysis over diel cycles. Such studies are limited because they underestimate rates of both release and uptake when they occur simultaneously, but they can provide information on the functional relationships of the different trophic components of the ecosystem when microbiological and chemical parameters are measured. Dissolved carbohydrates (CHO) are important bacterial substrates which are released by phytoplankton and macrophytes (Hellebust, 1974) and account for about 10 to 20% of the total dissolved organic carbon (DOC) in Narragansett Bay, Rhode Island, USA (Burney and Sieburth, 1977). Previous studies (Collier *et al.*, 1953; Walsh, 1965) have indicated large diel CHO fluctuations in inshore waters. The purpose of this study was to estimate net CHO release and uptake rates and to look for evidence of biological regulation of the CHO dynamics using measurements made at 2- or 3-h intervals over diel cycles from a New England salt marsh and a 5-m deep seawater tank designed to simulate the Narragansett Bay estuary.

Materials and Methods

The salt marsh sampling was conducted at a 6000 m² marsh embayment north of Bissel Cove on the West

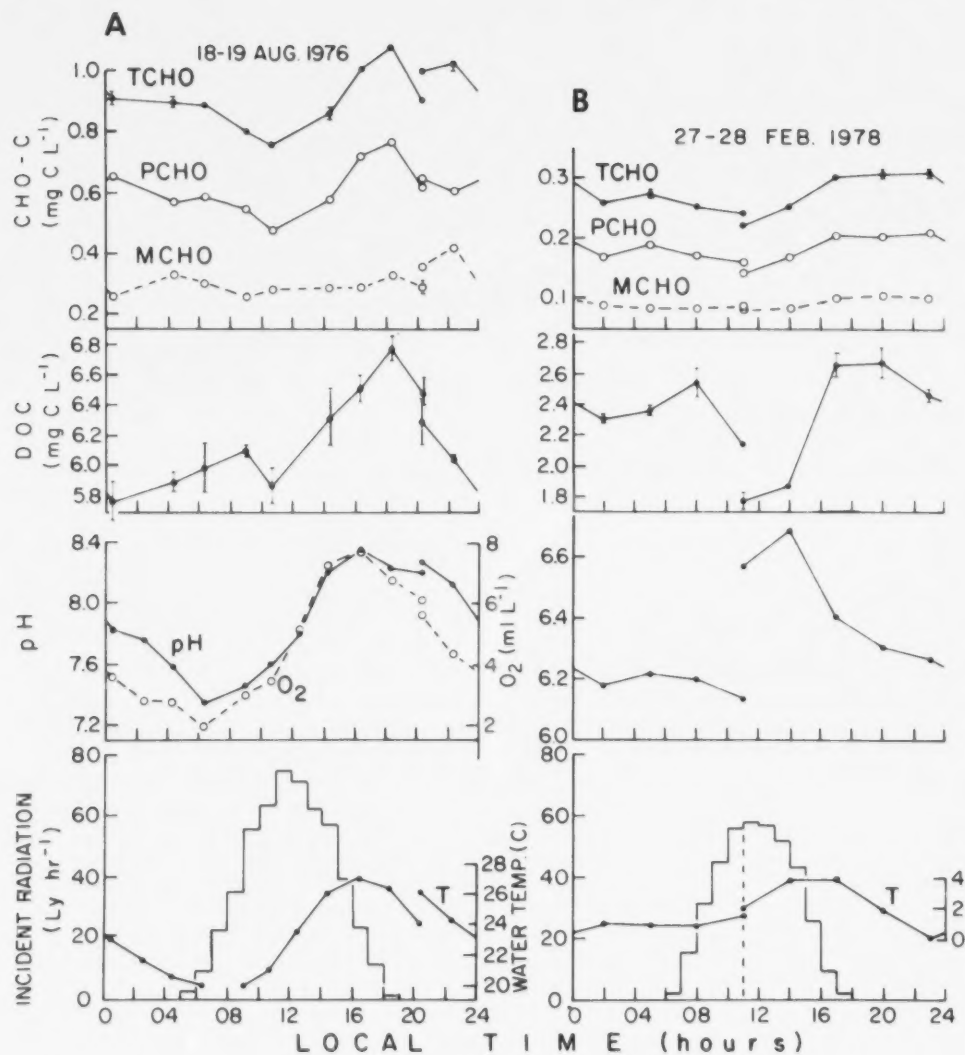


Fig. 1. Comparison of four multi-parameter diel studies on the Bissel Cove salt marsh

Passage of Narragansett Bay, Rhode Island. The area has been extensively described (Nixon and Oviatt, 1973; Nixon *et al.*, 1976). The principal advantage of this location for diel studies is that all tidal exchange with Bissel Cove can be blocked by plugging a culvert, thus trapping a water mass in which to conduct time series measurements. A total of six 24-h samplings were conducted from shore near the plugged culvert in the deepest part of the embayment (maximum of 1m) on 18-19 August 1976 and 27-28 February, 12-14 August, 30-31 August and 11-12 October 1978. Because of the level of the culvert, the study area normally receives flushing only during the upper third of the tidal cycle and the ecosystem is therefore accli-

mated to slack periods. During many 24-h studies, Nixon and Oviatt (1973) found no indication of any consistent changes in system metabolism associated with the length of time the culvert remained closed.

The simulated estuarine ecosystem was control tank No. 5 of the Marine Ecosystems Research Laboratory (MERL) at the Narragansett Bay campus of the University of Rhode Island (Pilson *et al.*, 1977). The tank holds a 5-m column of seawater above a 30-cm layer of Narragansett Bay sediment. Seawater is pumped from the bay at a rate of $0.48 \text{ m}^3 \text{ d}^{-1}$ to replace the tank volume every 27 d and tidal resuspension of particulate matter is simulated by intermittent mechanical mixing. Four diel studies were conducted on 3-4 March and 19-20

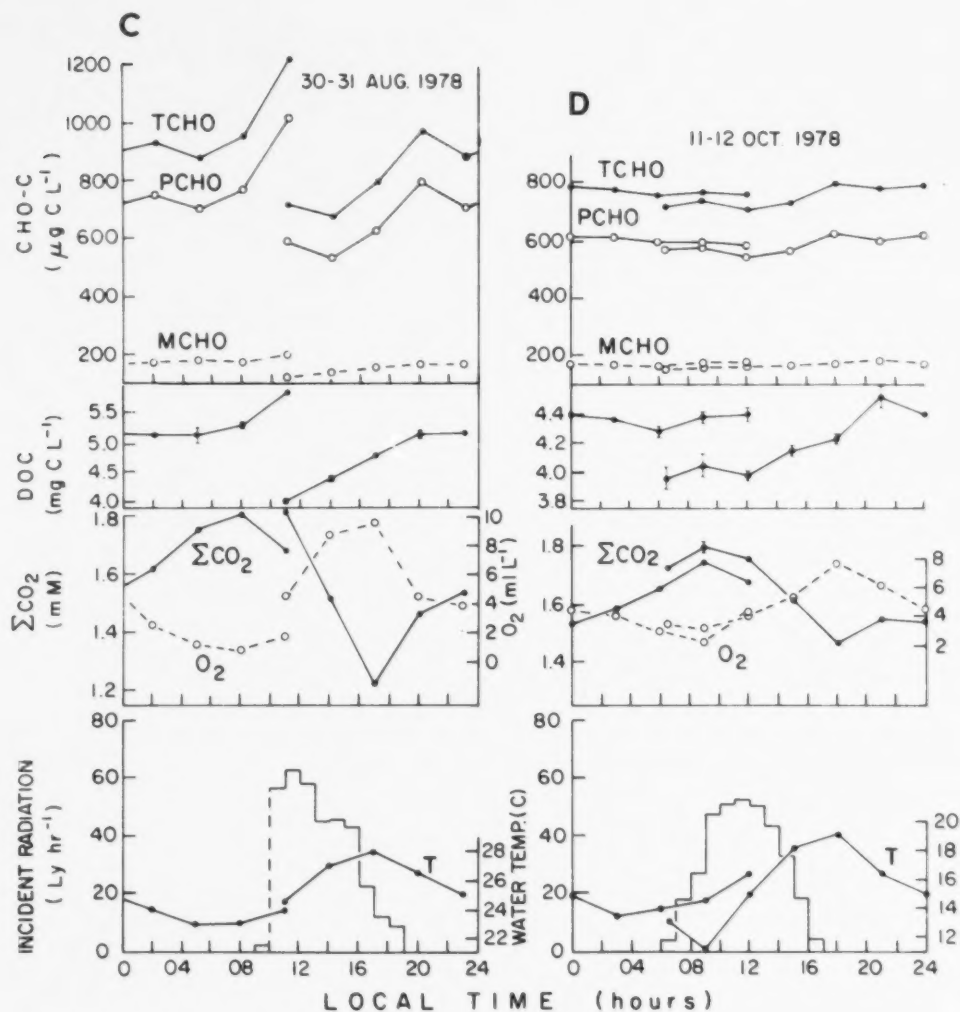


Fig. 1. (continued)

September 1977, 3-4 February 1978 and 6-7 June 1979. For the last study, the tank was operated in batch mode.

Samples were taken every 2 or 3 h from a depth of 1 m in the tank and just below the surface in the marsh. For oxygen, total carbon dioxide (ΣCO_2) and pH analyses, BOD bottles were filled by bubble-free siphon from the tank and with a 50-ml syringe from the marsh. The bottles were overflowed by several volumes and stoppered without bubbles. Other samples were collected in clean glass bottles mounted on a Wheaton (Millville, New Jersey) extension sampler which allowed them to be opened and closed below the surface to avoid contamination from the surface film (DiSalvo, 1973).

The samples were shielded from direct sunlight and returned to the laboratory where processing commenced within 15 min.

CHO and DOC samples were filtered by gravity through Gelman A/E glass fiber filters into glass bottles and frozen at -30°C . The filter holders were acid cleaned and pre-rinsed with sample. About 150 ml of sample was filtered and discarded before the aliquot for analysis was collected. All filters and sample bottles were precombusted at 450°C overnight. Monosaccharide (MCHO) was analyzed by the spectrophotometric MBTH method of Johnson and Sieburth (1977) using 0.025 M periodic acid ($0.57 \text{ g (100 ml)}^{-1}$ distilled water) instead of the $57 \text{ g (100 ml)}^{-1}$ concentration

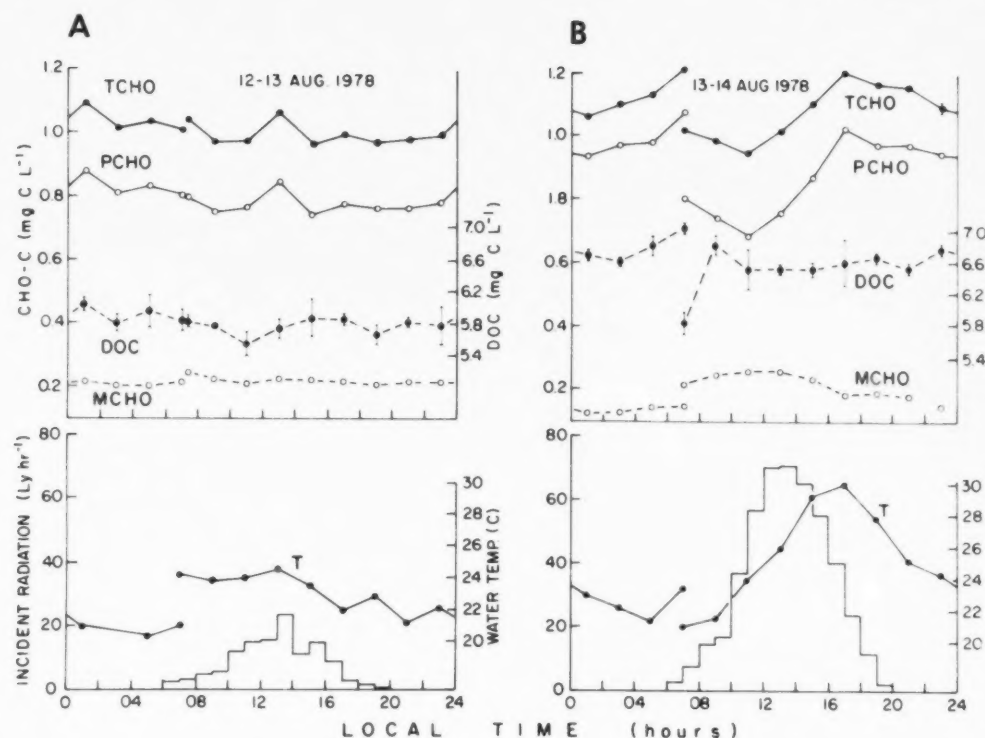


Fig. 2. Comparison of diel cycles of dissolved carbohydrates and DOC observed on consecutive cloudy and sunny days in the Bissel Cove salt marsh

erroneously specified in the above reference. Total dissolved carbohydrate (TCHO) was similarly determined on hydrolyzed samples and polysaccharide (PCHO) was estimated, according to Burney and Sieburth (1977). Four to six replicates were run for each analysis. Three to five DOC replicates per sample were analyzed by the wet persulphate oxidation method of Menzel and Vaccaro (1964) as modified by Kerr and Quinn (1975) using an Oceanography International (College Station, Texas) ampule analyzer panel and a Beckman (Fullerton, California) 315 infrared gas analyzer. After October 1978, an Oceanography International total carbon system, model 524B, was used. The output of both analyzers was integrated with an Infotronics model CRS-208 automatic digital integrator (Columbia Scientific, Houston, Texas).

In the first two salt marsh studies, CO₂ flux was estimated from pH measurements (Corning model 101 digital electrometer, Corning, New York) by the Beyers (1963) method using empirical pH-CO₂ curves obtained by titrating natural water samples with saturated CO₂ solutions. In later work, ΣCO₂ was determined directly by purging acidified samples with nitrogen and determining CO₂ by infrared analysis using the same equipment as for DOC (Johnson *et al.*, in press).

Dissolved oxygen was determined by the Winkler method (Carritt and Carpenter, 1966) except in the first marsh study when a Yellow Springs (Yellow Springs, Ohio) model 51A oxygen meter was used. In the MERL work, particulate chlorophyll *a* and phaeopigments were determined fluorometrically on 90% acetone extracts (Strickland and Parsons, 1968) using an Aminco (Silver Spring, Maryland) fluorocolorimeter. They were not determined in the marsh since plankton usually account for a small fraction of total system metabolism (Nixon and Oviatt, 1973). Salinity and temperature were measured with a hand refractometer and mercury thermometer, respectively. Integrated hourly solar radiation data from a roof-top pyrheliometer were provided by Eppley Laboratory in Newport, Rhode Island. For the last MERL study, suspended bacteria were counted using acridine orange staining and epifluorescence microscopy (Hobbie *et al.*, 1977).

Net apparent daily rates of release and uptake of TCHO, DOC, ΣCO₂ and O₂ were calculated from the time series data by the single diurnal curve method of Odum and Hoskin (1958). The calculation involves integration of the area under hourly rate of change plots. The positive area represents net input and the negative portion is proportional to net uptake. Hourly

Table 1. Daily and overall means for CHO and DOC values ($\pm$ one standard deviation) obtained in the Bissel Cove salt marsh and the MERL tank diel studies

Survey dates	$\mu\text{g C l}^{-1}$			
	TCHO $\pm$ SD	PCHO $\pm$ SD	MCHO $\pm$ SD	DOC $\pm$ SD
Salt Marsh				
18-19 Aug 1976	920 $\pm$ 100	613 $\pm$ 80	307 $\pm$ 47	6 190 $\pm$ 314
27-28 Feb 1978	268 $\pm$ 31	178 $\pm$ 23	90 $\pm$ 9	2 310 $\pm$ 326
12-13 Aug 1978	1 009 $\pm$ 41	793 $\pm$ 40	216 $\pm$ 10	5 800 $\pm$ 123
13-14 Aug 1978	1 096 $\pm$ 84	910 $\pm$ 121	186 $\pm$ 50	6 670 $\pm$ 160
30-31 Aug 1978	898 $\pm$ 161	729 $\pm$ 140	170 $\pm$ 23	5 000 $\pm$ 541
11-12 Oct 1978	755 $\pm$ 30	587 $\pm$ 25	168 $\pm$ 9	4 240 $\pm$ 189
MERL				
03-04 Mar 1977	284 $\pm$ 16	150 $\pm$ 14	134 $\pm$ 12	1 370 $\pm$ 127
19-20 Sep 1977	301 $\pm$ 15	201 $\pm$ 19	100 $\pm$ 17	2 413 $\pm$ 256
03-04 Feb 1978	185 $\pm$ 11	126 $\pm$ 9	59 $\pm$ 6	1 468 $\pm$ 68
06-07 Jun 1979	422 $\pm$ 31	323 $\pm$ 27	99 $\pm$ 9	1 597 $\pm$ 41
Overall				
Bissel Cove	849 $\pm$ 81	655 $\pm$ 80	194 $\pm$ 30	5 170 $\pm$ 279
MERL	308 $\pm$ 20	212 $\pm$ 19	96 $\pm$ 8	1 780 $\pm$ 150

Table 2. Daily and overall mean contributions of TCHO to DOC and of PCHO to TCHO in Bissel Cove salt marsh and the MERL tank

Survey dates	TCHO/DOC $\pm$ SD	PCHO/TCHO $\pm$ SD
Salt Marsh		
18-19 Aug 1976	0.149 $\pm$ 0.013	0.666 $\pm$ 0.038
27-28 Feb 1978	0.117 $\pm$ 0.010	0.664 $\pm$ 0.015
12-13 Aug 1978	0.174 $\pm$ 0.006	0.786 $\pm$ 0.012
13-14 Aug 1978	0.164 $\pm$ 0.012	0.827 $\pm$ 0.058
30-31 Aug 1978	0.179 $\pm$ 0.015	0.810 $\pm$ 0.015
11-12 Oct 1978	0.178 $\pm$ 0.005	0.778 $\pm$ 0.009
MERL		
03-04 Mar 1977	0.208 $\pm$ 0.020	0.528 $\pm$ 0.038
19-20 Sep 1977	0.126 $\pm$ 0.013	0.688 $\pm$ 0.035
03-04 Feb 1978	0.126 $\pm$ 0.008	0.679 $\pm$ 0.026
06-07 Jun 1979	0.264 $\pm$ 0.017	0.765 $\pm$ 0.019
Overall		
Salt Marsh	0.161 $\pm$ 0.023	0.758 $\pm$ 0.071
MERL	0.181 $\pm$ 0.064	0.677 $\pm$ 0.083

Table 3. Correlation coefficients and levels of significance (one tailed *t* test) between MCHO, PCHO and DOC

Survey dates	MCHO vs PCHO		PCHO vs DOC		MCHO vs DOC	
Salt Marsh						
18-19 Aug 1976	0.1845	n/s	0.6881	0.010	0.0957	n/s
27-28 Feb 1978	0.8590	0.002	0.8061	0.004	0.7345	0.012
12-13 Aug 1978	-0.0529	n/s	0.5302	0.031	0.0843	n/s
13-14 Aug 1978	-0.8246	<0.001	0.4200	n/s	-0.4447	n/s
30-31 Aug 1978	0.8712	0.001	0.8973	<0.001	0.9905	<0.001
11-12 Oct 1978	0.3981	n/s	0.6857	0.010	0.7615	0.003
MERL						
03-04 Mar 1977	-0.2520	n/s	-0.4014	n/s	0.4516	n/s
19-20 Sep 1977	-0.7312	0.002	0.1839	n/s	0.0721	n/s
03-04 Feb 1978	-0.1794	n/s	0.3182	n/s	0.1541	n/s
06-07 Jun 1979	0.2510	n/s	0.4574	n/s	0.5641	0.022

n/s listed when $P > 0.05$

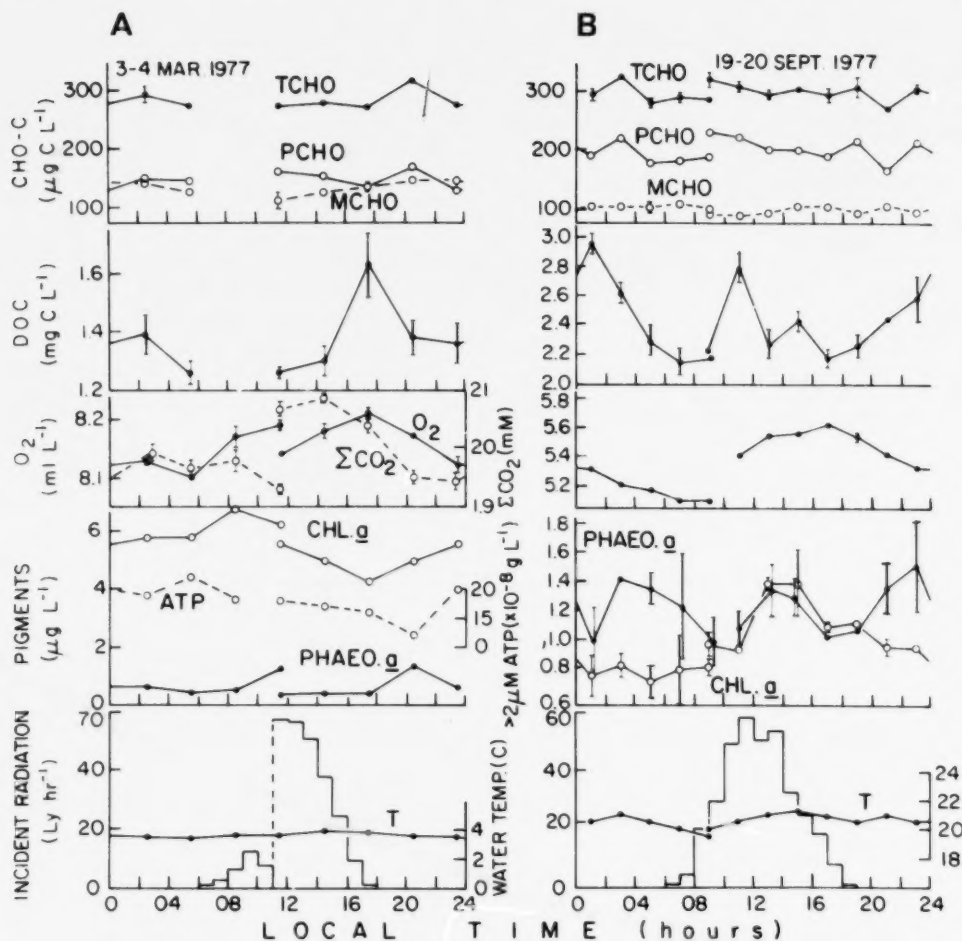


Fig. 3. Comparison of four multi-parameter diel studies on the MERL simulated estuarine ecosystem (control tank No. 5)

oxygen rates were corrected for atmospheric exchange using empirical reaeration constants of 0.28 and 0.012 ml O_2 $l^{-1}h^{-1}$ (determined at a 100% air-water saturation deficit) for the marsh and tank data, respectively (S. Nixon, personal communication). Rates for ΣCO_2 were not corrected for atmospheric diffusion since this is insignificant relative to biological flux in areas of high productivity (Smith, 1973; Johnson *et al.*, 1979). Oxygen flux was expressed in terms of carbon by assuming that 1 ml of O_2 represents 536 μg C ($PQ = RQ = 1$).

Results

Fig. 1 presents the results of four multi-parameter diel studies on the Bissel Cove salt marsh. Data from

two less extensive observations in the marsh (Fig. 2), made on consecutive days, show the effects of a cloudy and sunny day. Fig. 3 gives the results of four multi-parameter diel studies in the MERL tank. To facilitate comparisons, a standardized time scale (abscissa) was used in these figures, with 12:00 noon centrally located. This causes a break in the curves with the right and left segments representing the first and second day of each study, respectively. Error bars representing plus and minus one standard error from the mean were plotted on the TCHO, MCHO, DOC, ΣCO_2 , O_2 , chlorophyll *a* and phaeopigment curves. When no bar appears, the standard error was smaller than the plot symbol. Fig. 4 illustrates the multiple linear relationships of the total TCHO and PCHO accumulations occurring between 10:40 and 20:00 hrs, with daily solar radiation and mean daily temperature, for the six marsh

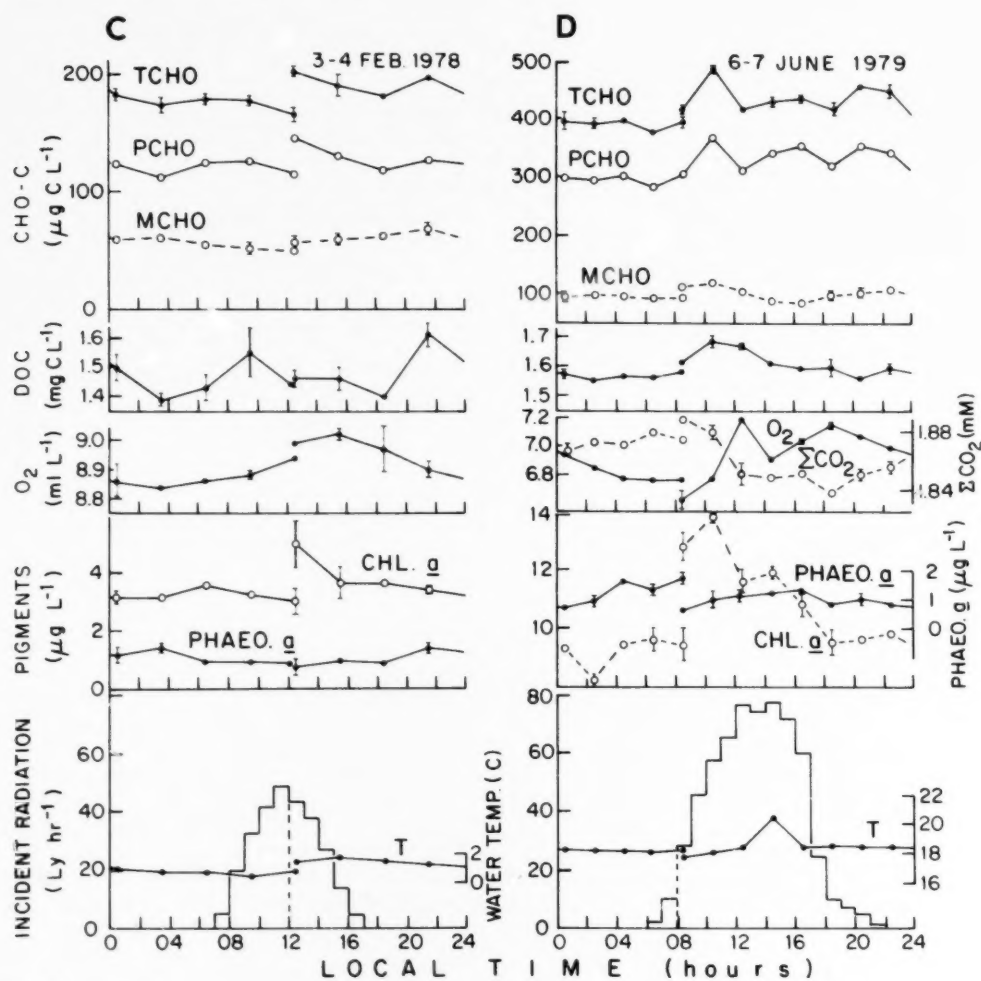


Fig. 3. (continued)

Table 4. Daily net apparent flux of CHO, DOC, O_2 and ΣCO_2 expressed as $\mu\text{g C l}^{-1} \text{d}^{-1}$

Dates	TCHO R/U	DOC R/U	O_2 P/R	CO_2 P/R
Salt Marsh				
18 Aug 1976	293/419	907/964	2743/2974	2685/3411
02 Feb 1978	88/65	1008/638	n	n
12 Aug 1978	189/214	620/610	n	n
13 Aug 1978	370/168	1559/359	n	n
30 Aug 1978	520/173	1559/275	2027/4975	7540/5956
11 Oct 1978	85/45	551/176	2102/2550	3604/2823
MERL				
03 Mar 1977 ^a	39/31	291/245	87/42	1657/495
19 Sep 1977	54/87	1240/1190	107/267	n
03 Feb 1978	16/40	174/184	69/89	n
06 Jun 1979	109/131	108/143	348/273	625/459

R/U = Release/uptake

P/R = Production/respiration

a = Integrated over 18 h only

n = no data

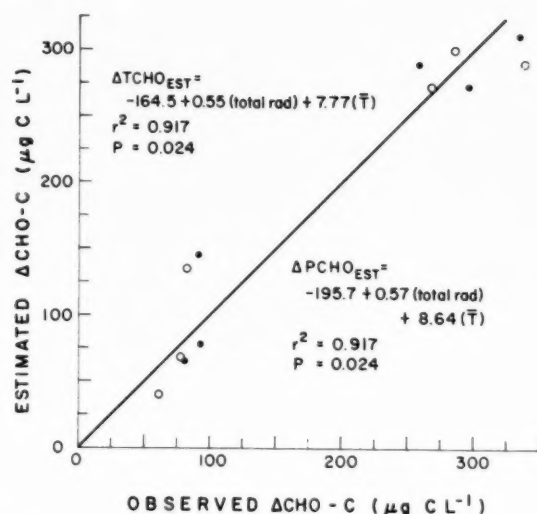


Fig. 4. The total observed TCHO (closed circles) and PCHO (open circles) accumulation occurring between 10:40 and 20:00 hrs in the six marsh studies as a function of the estimated rates (EST) derived from multiple linear relationships incorporating daily solar radiation (total rad, ly d⁻¹) and mean daily temperature (T °C). The line represents a perfect 1:1 relationship

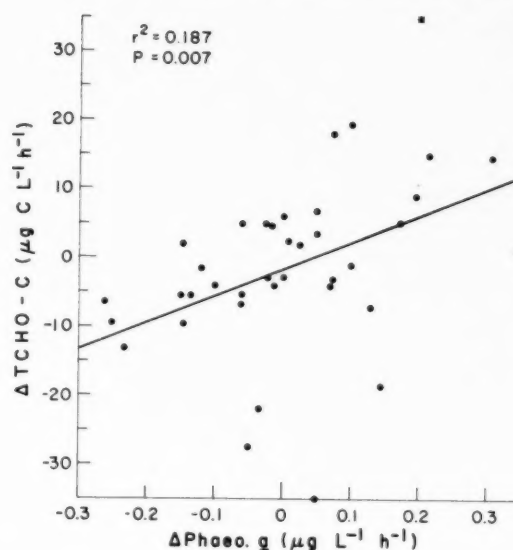


Fig. 5. Correlation of the rates of change of TCHO and phaeopigment fluctuations in the combined data from the four MERL tank studies

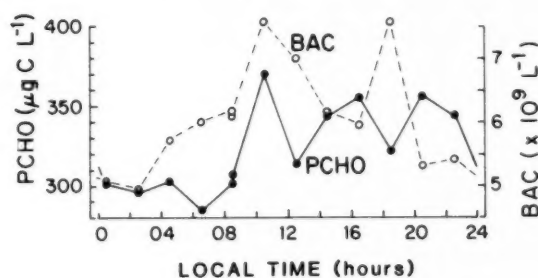


Fig. 6. Comparison of the diel patterns of PCHO and BAC in MERL tank No. 5, 6-7 June 1979

studies. Fig. 5 shows the direct relationship between phaeopigment and TCHO fluctuations in the combined MERL data. Fig. 6 compares bacterial populations and PCHO concentrations in the June MERL study.

Table 1 lists the mean TCHO, PCHO, MCHO and DOC values ($\pm$ one standard deviation) for each diel cycle and the overall values for both locations. The mean contributions of TCHO to DOC and of PCHO to TCHO are presented for each study in Table 2. Correlation coefficients and significance levels derived from the MCHO, PCHO and DOC data are given in Table 3. PCHO and TCHO were always positively correlated ($P < 0.005$) except for the first MERL study where $P = 0.052$. The daily net apparent flux of TCHO and DOC with total system net production

and respiration estimates based on the O₂ and CO₂ data for both the salt marsh and MERL tank are summarized in Table 4. The daily net rates of TCHO release and uptake compared to those for DOC and Σ CO₂ based production and respiration for both the marsh and MERL tank are given in Table 5.

Discussion

Results from each of the salt marsh studies in Fig. 1 show evidence of highly significant TCHO accumulation, primarily due to net PCHO release, commencing in the late morning or early afternoon and continuing through at least two sampling periods into the early evening. Except for the 30-31 August 1978 study (Fig. 1-C), TCHO and PCHO usually reached their daily maxima at the end of this period. The maximum rates of PCHO accumulation in this time period occurred during or just after the period of maximum net system production indicated by the O₂, pH and Σ CO₂ data (Fig. 1).

No period of PCHO accumulation was sustained over more than one sampling interval during a cloudy day in August (Fig. 2-A), however a very pronounced PCHO increase from 11:00 to 17:00 hrs appeared on the following clear day (Fig. 2-B), suggesting an association between the photosynthetic rate and PCHO release. PCHO release on the cloudy day was probably curtailed due to light limitation of photosynthesis. Morris and Skeggs (1978) have shown that sub-optimal

Table 5. Daily net TCHO rates as percentages of DOC flux and net apparent system production based on ΣCO_2 flux

Date	TCHO release	TCHO uptake	TCHO release	TCHO uptake
	DOC release percent	DOC uptake percent	Production percent	Respiration percent
Salt Marsh				
8/18/76	32	43	11	12
2/27/78	9	10	n	n
8/12/78	30	35	n	n
8/13/78	24	47	n	n
8/30/78	33	63	7	3
10/11/78	15	26	2	2
MERL				
3/03/77	13	13	2	6
9/19/77	4	7	n	n
2/03/78	9	22	n	n
6/06/79	101	92	17	29

n = no data

light intensities cause phytoplankton to incorporate a smaller fraction of their photoassimilated carbon into PCHO. For the six marsh studies, total TCHO and PCHO accumulations in the 10:40 to 20:00 hrs time period were significant functions of daily solar radiation and mean daily temperature (Fig. 4). This direct association with solar radiation suggests that these accumulations resulted from net release of recently fixed PCHO.

The recent photosynthetic origin of the PCHO which accumulates through the afternoon in the marsh is indicated, but the mechanism causing its extracellular release is unknown. Phytoplankton and macroalgae contain maximal cellular CHO levels in the afternoon (Gibson, 1978; Oohusa *et al.*, 1978) when a large proportion of their photosynthate is incorporated into PCHO (Morris and Skea, 1978). Its release during this time may be due to leakage or excretion of excess PCHO storage product. During two summer marsh studies, periods of sustained PCHO release occurred in the morning from 05:00 to 11:00 hrs (Fig. 1-C) and from 01:00 to 07:00 hrs (Fig. 2-B). These early morning accumulations did not occur consistently and their source is unknown but they probably result from different processes than those responsible for the afternoon-evening PCHO peaks, such as excretion by *Palaeomonetes pugio* (Johannes and Satomi, 1967) or other consumers.

The MCHO cycles in the marsh (Figs. 1 and 2) show much smaller net fluctuations relative to PCHO. Simple sugars are usually not major extracellular products of algae (Hellebust, 1974) and may be maintained at or near the threshold concentration for heterotrophic uptake by the bacterial populations (Jannasch, 1967). It is also quite possible that actual MCHO flux was much greater than our data indicate because of simultaneous release and uptake producing only small net changes. If this occurs, it requires a very close coupling between these processes as reported by Wiebe and Smith (1977) and Larsson and Hagström (1979).

The MERL tank (Fig. 3) did not show large PCHO and TCHO excursions as did the marsh. There was also a lack of the sustained afternoon PCHO increases which were characteristic of the marsh. This may be due to lower net system production in the tank or to increased bacterial activity in the afternoon and evening which may prevent CHO accumulation. There was some suggestion of the latter possibility in the June MERL study in which bacterial numbers were inversely related ($r = -0.856$, $P = 0.030$) to PCHO concentrations during the afternoon and evening (Fig. 6) suggesting that bacterial uptake was the dominant process determining PCHO levels. During this period, increasing bacterial populations caused PCHO reductions, and declining bacterial numbers, due to death or consumption, allowed PCHO accumulation because of ongoing release from phytoplankton and zooplankton. During the late morning, the bacteria apparently responded to a large PCHO pulse which temporarily exceeded their uptake capacity producing concurrent peaks. The size of the bacterial population, which was not consistently related to the mixing schedule of the tank (2 h on, 4 h off commencing at 08:30 hrs) appeared to be closely coupled to natural substrate levels during much of the day. Such close coupling over short time intervals has been previously suggested by studies on the rates of phytoplankton release and bacterial uptake (Wiebe and Smith, 1977; Larsson and Hagström, 1979) and by another diel study (Meyer-Reil *et al.*, 1979). Lack of a consistent PCHO-bacteria relationship in the early morning hours (Fig. 6) probably does not indicate bacterial inactivity but more likely a diminished rate of PCHO input allowing concentrations to decline to low levels. Apparent bacterial growth during this time may have been at the expense of other substrates.

The significant direct relationship between the apparent rates of change of phaeopigments, which result from metazooplankton excretion (Lorenzen,

1967; Shuman and Lorenzen, 1975), and TCHO in the tank (Fig. 5) suggests the importance of zooplankton mediated release of phytoplankton produced CHO in this simulated estuarine ecosystem. Metazooplankton are known to release DOC through their excretion and sloppy feeding (Conover, 1966; Lampert, 1978). Protozooplankton excretion appears to influence vertical CHO profiles in the North Atlantic (Burney *et al.*, 1979).

As expected, the overall mean CHO and DOC concentrations (Table 1) were 2 to 3 times higher in the salt marsh than in the MERL tank. Both systems also followed a seasonal pattern with the highest concentrations in summer, lowest in winter and intermediate levels in the fall samples, although MCHO and DOC deviated slightly from this in the MERL tank. The overall contribution of TCHO to the total DOC was significantly larger ($P = 0.012$) in the tank than in the marsh even though the September and February MERL values were lower than most of those from the marsh (Table 2). TCHO carbon accounted for more than 20% of the DOC in the tank in the March and June surveys. The tank also contained significantly higher chlorophyll *a* concentrations on these dates indicating that the increased proportion of TCHO in the DOC may have been associated with the increased phytoplankton biomass. The TCHO was composed primarily of PCHO in all studies (Table 2) which accounted for slightly over half to more than 80% of the total. Overall, a significantly larger ($P < 0.001$) fraction of the TCHO was polymerized in the salt marsh than in the MERL ecosystem which agrees with the findings of Wheeler (1976) and the higher proportion of PCHO found near land in the North Atlantic (Burney *et al.*, 1979).

A significant ($P < 0.05$) positive correlation between PCHO and DOC occurred in all but one of the marsh investigations (Table 3) but in none of the MERL studies. In the marsh, other organic compounds apparently follow patterns of release and uptake similar to that of PCHO, while in the MERL tank other types of organic matter seem to fluctuate independently. MCHO showed no consistent correlation with DOC in either location, however significant positive relationships occurred three times in the marsh and once at MERL. The factors which cause the apparent coupling of MCHO and DOC fluctuations in some instances and not in others remain obscure.

The relation of MCHO to PCHO (Table 3) was also variable. When significance was achieved, the confidence levels were very high and some of the correlations were inverse. Inverse variations of these constituents occurred to some extent in all 10 studies, regardless of the overall correlation coefficients (Figs. 1 to 3). This may be due in part to interconversion of PCHO and MCHO. PCHO can be converted to MCHO through bacterial extracellular enzymatic hydrolysis (Khailov, 1968). Bacteria can also assimilate MCHOs and rapidly excrete large molecules made from them (Nalewajko and Lean, 1972; Dunstall and Nalewajko, 1975). Of course, interconversion cannot account for all of the opposite variation in MCHO and PCHO, especially

when one increases more than the other declines. The effect could be simply due to variations in the differential rates of biological release and uptake of the two components. However, the possibility of interconversion prevents the strict interpretation of their dynamics as net biological release and uptake.

This ambiguity does not apply to TCHO fluctuations which frequently corresponded to summer release and uptake rates exceeding $30 \mu\text{g C l}^{-1}\text{h}^{-1}$ in the marsh and $20 \mu\text{g C l}^{-1}\text{h}^{-1}$ in the tank, assuming non-biological processes were insignificant on the time scales involved. Spatial heterogeneity was probably not a problem in either the mixed MERL tank or in the marsh which lacked significant advective processes when the culvert was plugged. CHO dynamics at our sampling station in the marsh were probably controlled by temporal processes of the biota in the immediate area, but rates in other parts of the marsh may well have been different. Our values are not claimed to be representative of the entire $6\,000 \text{ m}^2$ area.

Most of the previous data on carbohydrate uptake has been generated with the heterotrophic potential method (Parsons and Strickland, 1962; Wright and Hobbie, 1966) employing a Michaelis-Menten kinetic treatment and usually ^{14}C -glucose. Maximum uptake velocities (V_m) of about $10 \mu\text{g C l}^{-1}\text{h}^{-1}$ from polluted areas and about $5 \mu\text{g C l}^{-1}\text{h}^{-1}$ from unpolluted waters have been reported (Hoppe, 1978; Hobbie, 1979). These are far below the maximal rates of apparent TCHO uptake of 98 and $35 \mu\text{g C l}^{-1}\text{h}^{-1}$ suggested by the largest fluctuations observed in the marsh (Fig. 1-A) and tank (Fig. 3-D), respectively. However, the two methods are so different that these data are hardly comparable. Ignoring the serious technical problems (Wright, 1973) and reservations concerning the applicability of the Michaelis-Menten model to mixed natural systems (Gocke, 1977; Krambeck, 1979) which places literal quantitative interpretation of the kinetic parameters in serious doubt (Bell, 1980), the heterotrophic potential method purports to measure gross bacterial uptake of the added substrate when correction is made for respired $^{14}\text{CO}_2$. Newer methods measuring uptake of ^{14}C or ^3H labeled glucose without a Michaelis-Menten approach (Dietz *et al.*, 1976; Meyer-Reil *et al.*, 1978) avoid this problem but still estimate the flux of only a fraction of the natural substrate. In contrast to this, rates from *in-situ* time series measurements estimate the net CHO release and uptake of the entire ecosystem. Any CHO release during a period of net uptake is not measured and contributes to the underestimation of actual uptake and vice versa. However, this approach is advantageous in systems lacking significant advection because there are no bottle incubations and the flux of an entire class of naturally occurring substrates rather than of a single added compound or externally produced mixture is estimated. Therefore, we believe that flux estimates using this method provide more ecologically meaningful, if somewhat underestimated, results.

Daily rates of TCHO release and uptake in the salt marsh (Table 4) ranged from 85 to 520 $\mu\text{g C l}^{-1}\text{d}^{-1}$ and 45 to 419 $\mu\text{g C l}^{-1}\text{d}^{-1}$, respectively, with lower rates in the fall and winter than in summer. Walsh (1965) calculated TCHO release equivalent to 265 $\mu\text{g C l}^{-1}\text{d}^{-1}$ in a 2 m basin of a productive coastal pond (August) which is in the range of our summer values. TCHO flux on a volume basis in the MERL tank was considerably lower than in the marsh, ranging from 16 to 109 $\mu\text{g C l}^{-1}\text{d}^{-1}$ for net release and 31 to 131 $\mu\text{g C l}^{-1}\text{d}^{-1}$ for net uptake. Because water depth in the tank was about 5 times that at the marsh station, on a m^2 basis, the range of release values in the two systems were similar and the range of uptake rates was higher in the tank than the marsh.

The estimates of net daily production and respiration (Table 4) present a problem. Although several studies are in fair agreement, all of the values based on ΣCO_2 flux exceed (sometimes drastically) those based on O_2 rates. This happened even in the last MERL survey and all of the marsh studies where ΣCO_2 (or pH) and O_2 showed the expected highly significant ($P < 0.01$) correlations. The discrepancy was greatest in the first MERL investigation (Fig. 3-A) where unknown processes caused O_2 and ΣCO_2 to vary directly through much of the study. These results may have been due to chemosynthesis, anaerobic processes in the sediments or possibly to differences in the kinetics of O_2 and ΣCO_2 uptake in fluctuating light regimes (Gallegos *et al.*, 1980). We believe the values based on ΣCO_2 measurements to be more accurate since CO_2 is less affected by atmospheric exchange (Smith, 1973; Johnson *et al.*, 1979) than is oxygen, and ΣCO_2 rates do not require the assumption of photosynthetic and respiratory quotients for conversion to carbon units. This subject will be discussed in more detail elsewhere (Johnson *et al.*, in press).

In the salt marsh, net daily TCHO release accounted for 9 to 33% of the net DOC release and 10 to 63% of the DOC uptake (Table 5), with the largest fractions found in summer, smallest in winter, and intermediate values in fall. Net TCHO release amounted to 2–11% of the net system production based on CO_2 flux. Walsh (1965) estimated that from 14 to 44.9% of assimilated carbon was released as TCHO in Oyster Pond (summer), however his O_2 based production values were considerably lower than our ΣCO_2 based values. We estimate that daily TCHO uptake accounted for 2 to 12% of the net system respiration in the marsh.

The contribution of TCHO to the daily DOC flux showed extreme seasonal variability in the MERL tank (Table 5). TCHO accounted for from 4 to 101% of the net DOC release and from 7 to 92% of its net uptake. Values exceeding 100% are possible and indicate that another important fraction of the DOC varied inversely with the TCHO over part of the study. This lack of a direct apparent coupling of the DOC and TCHO flux in the simulated estuary appears to indicate a functional dissimilarity between this system and the marsh. The June rates of net TCHO release and uptake

in the tank (Table 5) constituted the largest fractions of the net production and respiration found in any of the studies at either location. The low molar ratios of nitrate plus ammonia to phosphate (0.5 to 2.6) in this study (C. M. Burney, unpublished data) may indicate nitrogen limitation which is known to increase CHO excretion by phytoplankton (Myklestad and Haug, 1972).

The multi-parameter diel sampling of confined water masses at 2- to 3-h intervals can yield useful information on the interaction of ecosystem components as well as on their net rates of change. As discussed by Sournia (1974), the ecological significance of fluctuations over diel cycles may be at least as important as those over annual periods. This study sought to contribute to our knowledge of the role of dissolved organic matter in the sea by studying the *in situ* diel flux of one of its biologically labile constituents.

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